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OUP, LLC  
te.com  
St., 5th Floor  
CA 94107  
512-8800  
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30 AUSTRIA, BELGIUM, GERMANY, SPAIN, UNITED KINGDOM, ITALY, THE  
NETHERLANDS
- (71) Applicant: INSTITUT FRANCAIS DU PETROLE [FRENCH PETROLEUM  
INSTITUTE]  
4, avenue de Bois-Préau  
35 F-92502 Ruell-Malmaison (FRANCE)
- (72) Inventor: Bernard Juguin  
Deceased (FRANCE)  
Inventor: Jean-François Joly  
40 20, rue Béranger  
F-75003 Paris (FRANCE)  
Inventor: Francis Raatz  
25, rue de la Carrière



F-57500 Saint Avoir (FRANCE)  
Inventor: Germain Martino  
Bât. Condé, 80, avenue F. Lefebvre  
F-78300 Poissy (FRANCE)  
Inventor: Philippe Caullet  
4, rue Kellermann  
F-68110 Ilizach (FRANCE)

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10 (54) **Process for the production of 2-phenylalkanes and 3-phenylalkanes using a catalyst that is based on a special mordenite**

15 (57) Process for the production of a mixture of 2-phenylalkanes and 3-phenylalkanes in which benzene is made to react with a charge, which contains at least one linear olefin that comprises 9 to 16 atoms of carbon in its molecule and that is in contact with a catalyst that is based on a mordenite that has an overall Si/Al atomic ratio of between 6 and 100 and, preferably, between 15 and 60, whereby the said mordenite was prepared from a mordenite that had been synthesized in a fluoride medium. [This patent application also claims the] use of the mixture of 2-phenylalkanes and 3-phenylalkanes, which is obtained, as a basis for biodegradable detergents.

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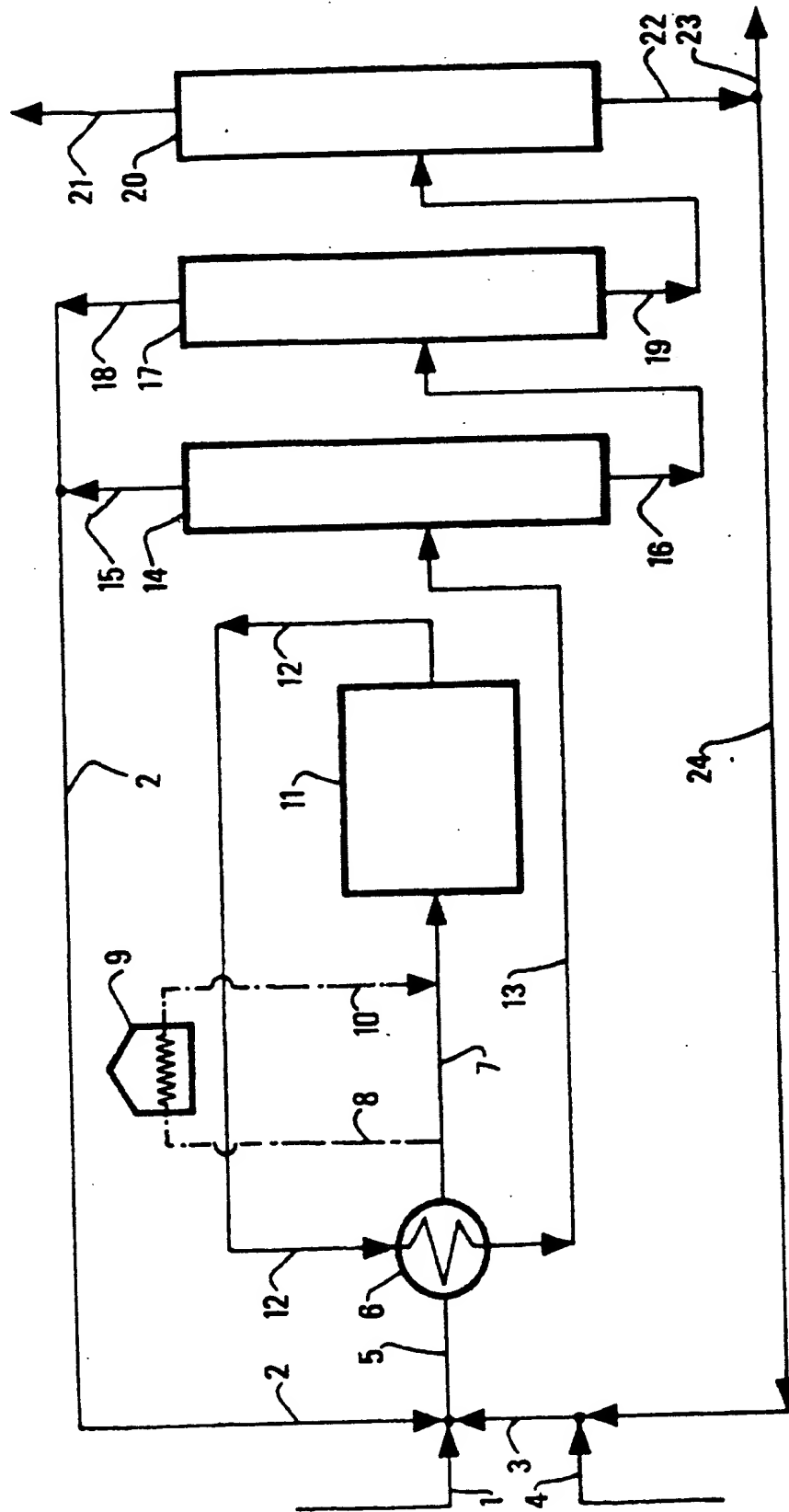
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The present invention pertains to a process for the production of 2-phenylalkanes and 3-phenylalkanes via the alkylation of benzene by means of linear olefin(s) that comprise 9 to 16 atoms of carbon and more particularly, 10 to 14 atoms of carbon, in the presence of at least one catalyst that is based on a special mordenite.

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The 2-phenylalkanes and 3-phenylalkanes that are obtained in accordance with the invention constitute compounds which, after sulfonation, are suitable for the formulation of biodegradable detergents.

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At the present time, the bases of biodegradable detergents largely make use of linear alkylbenzenes. The production of this type of compound is growing regularly: in terms of scale, it is approaching 650,000 metric tons/year in Western Europe, for example. In addition to their detergent power, one of the main properties that are sought in regard to these compounds, after the sulfonation step, is biodegradability. In order to ensure maximum biodegradability, the alkyl group has to be linear, and the distance between the sulfonate group and the terminal carbon of the linear chain should be maximal, and the phenyl group should be as close as possible to one of the ends of the alkyl group. Thus the linear alkylbenzenes of the 2-phenylalkane and 3-phenylalkane types are most suitable in order to achieve this objective, whereby the most interesting agents for the alkylation of benzene comprise C<sub>9</sub>-C<sub>16</sub> or, preferably, C<sub>10</sub>-C<sub>14</sub> linear

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olefins.

The linear alkylbenzenes that are obtained via the alkylation of benzene by means of linear olefin(s) are currently prepared using two major processes.

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The first process is licensed by UOP (B. Vora, P. Pujado, J. Spinner, T. Imal, Hydrocarbon Processing, Nov. 1984, p. 86; Petrochemical Handbook, Hydrocarbon Processing, Nov. 1987, p. 63). This process uses hydrofluoric acid as the catalytic agent during the benzene alkylation step.

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The second process is licensed by ARCO Technology, Inc. (Petrochemical Handbook, Nov. 1985, p. 127). The alkylation catalyst here is of the Friedel-Craft type, particularly on the basis of Al-C<sub>13</sub> [translator: AlCl<sub>3</sub> is presumably meant here].

These two processes exhibit several major disadvantages. One of the disadvantages results from the non-selectivity of the catalysts that are used in these processes. If, in fact, these catalysts are very selective from the alkylation point of view, then they lead to the formation of all the linear phenylalkanes that are possible. In addition to the 2-phenylalkanes and 3-phenylalkanes, the formation of 4-phenylalkanes, 5-phenylalkanes and 6-phenylalkanes takes place because of geometrical isomerization at the double bond of the initial olefin.

Another disadvantage relates to environmental restraints. The UOP process, which is based on the use of hydrofluoric acid, poses severe safety problems on the one hand and, on the other hand, of reprocessing the waste materials. The ARCO process poses the classical problem with processes that are based on Friedel-Craft catalysts, i.e. the problem of the effluent; for this type of process, in fact, it is necessary to neutralize the effluent, by means of a basic solution, when they leave the reactor. These various disadvantages compound the difficulties that are associated with the separation of the catalyst from the products of the reaction.

These various restraints explain the interest that there will be in perfecting a process for the alkylation of benzene via linear olefins in the presence of a solid catalyst that possesses geometrical selectivity properties that lead to improved selectivity with respect to 2-phenylalkanes and 3-phenylalkanes. On the one hand, such a catalytic formula would permit the elimination of problems in regard to the environment and in regard to catalyst/effluent separation and, on the other hand, it would permit maximization of the production of the 2-phenylalkanes and 3-phenylalkanes, i.e. the products that are primarily sought. Certain zeolites could constitute such solid catalysts with geometric selectivity. Thus the use of these types of solid for the alkylation of benzene has already been described in several publications. As early as 1973, Bowes (patent number US-A-3716596) claimed the use of a H-ZSM4 zeolite with a  $\text{SiO}_2/\text{Al}_2\text{O}_3$  molar ratio of 7.7. More recently, Young (patent number US-A-4301317) has claimed a whole series of zeolites for the alkylation of benzene via long linear olefins. The following are found, in particular, among the structures that are quoted by this author: cancrinite, gmelinite, mordenite, offretite [sic] and ZSM 12. Prior to use, these zeolites have to be transformed, at least partially, into their hydrogen form. The technique that is required in order to carry out this transformation comprises the replacement of the cations, which are initially present in the solid,

by precursors of protons, such as ammonium ions, followed by calcination of the ammonium form, which is thus obtained, in the presence of steam. The product that results from this initial transformation can then be subjected to various chemical treatments, particularly treatments to remove aluminum. The zeolites that are prepared in accordance with this technique (US-A-  
 5 4301317) exhibit quite good results for the alkylation of benzene via linear olefins that contain at least 5 atoms of carbon. The temperature that is required for the reaction should be greater than 50°C and the pressure should be greater than 1 MPa.

The applicant has discovered that mordenites, which are prepared from mordenites that  
 10 have been synthesized in a fluoride medium in accordance with the process for their preparation that is described and claimed in a French patent application with 89/13317 as its national registration number that was filed on October 10, 1989, exhibit properties that are particularly interesting for the alkylation of benzene by means of linear olefin(s) comprising 9 to 16 atoms of carbon, for example 10 to 14 atoms of carbon. Relative to the levels of performance of catalysts  
 15 that are prepared from mordenites that have been synthesized in a classical OH<sup>-</sup> medium, the catalysts that are prepared from the mordenites that have been synthesized in a fluoride medium (called raw synthetic mordenites) exhibit, in particular, superior levels of catalytic performance for the above-mentioned reaction in terms of the production of 2-phenylalkanes and 3-phenylalkanes. The said mordenites that are synthesized in a fluoride medium (called raw  
 20 synthetic mordenites) correspond advantageously to the mordenites that are described and claimed in the above French patent application 89/13317 of which a partial description is incorporated here by way of reference.

After its synthesis, the mordenite of approximate general formula  $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot x\text{SiO}_2$ ,  
 25 which is described and claimed in the said French patent application, is characterized, in particular, by:

- a/ a number x that is between 9 and 30 and, preferably, between 9 and 20 (x being the  $\text{SiO}_2/\text{Al}_2\text{O}_3$  molar ratio);
- 30 b/ an x-ray diffraction diagram that is illustrated in Table I of the specification of French patent application 89/13317, whereby the said Table I is reproduced below.

This raw synthetic mordenite is also characterized by the fact that it was synthesized in a fluoride medium.

The identification of the mordenites can be carried out with ease from their x-ray diffraction diagram. This diffraction diagram can be obtained with the help of a diffractometer by using the classical powder method via the K-alpha radiation from copper. An internal reference standard permits the determination of values of the angles  $2\theta$  that are associated with the diffraction peaks. The different interplanar distances  $d_{hkl}$ , which are characteristic of the sample, are calculated from the Bragg relationship. An estimate of the measurement error  $\delta(d_{hkl})$  is calculated as a function of the absolute error  $\delta(2\theta)$  that is assigned to the measurement of  $2\theta$  via the Bragg relationship. This error is minimized by the presence of an internal reference standard, and is currently taken to be equal to  $\pm 0.05^\circ$ . The relative intensity  $I/I_0$  that is assigned to each value of  $d_{hkl}$  is estimated from the height of the corresponding diffraction peak. The latter can also be determined from a photographic negative that is obtained with the help of a Debye-Scherrer chamber. Use is often made of a scale with symbols in order to characterize this intensity: FF = very strong; F = strong; mF = moderate to strong; m = moderate; mf = moderate to weak; f = weak; ff = very weak.

Table I represents the x-ray diffraction diagram that is characteristic of the mordenites in accordance with French patent application 89/13317. The extreme values that can be adopted by the different interplanar distances  $d_{hkl}$  are presented in the column for  $d_{hkl}$ . Each of these values should have assigned to it the measurement error  $\delta(d_{hkl})$  that is generally between  $\pm 0.07$  and  $\pm 0.002$  depending on the value of  $2\theta$  ( $d_{hkl}$  is expressed in Angstrom units;  $1 \text{ \AA} = 10^{-10} \text{ m}$ ).

The raw synthetic mordenite that was synthesized in a fluoride medium is advantageously prepared in accordance with the process that is described and claimed in French patent application 89/13317, whereby this is a procedure of which a partial description is reproduced below by way of reference:

5 a) a reaction mixture is formed in solution that has a pH that is less than approximately 10 and is preferably between approximately 4 and approximately 10 (and still more preferably between approximately 6 and approximately 10) and contains water, at least one source of silica, at least one source of aluminum, at least one source of a transforming agent that contains fluoride ions ( $F^-$ ), and a source of sodium cations ( $Na^+$ ), whereby the said reaction mixture has a composition, in terms of molar ratios, that is contained within the following ranges of values:

10 Si/Al: 5-50 and preferably 5-25, for example 6.5-15;  
F/Si: 0.1-10 and preferably 0.25-8, for example 0.4-5;  
Na<sup>+</sup>/Si: 0.1-10 and preferably 0.25-8, for example 0.4-5;  
H<sub>2</sub>O/Si: 5-25 and preferably 8-25, for example 8-22;

15 b) the said reaction mixture is maintained at a temperature that has been elevated by heating, namely to between approximately 90 and approximately 250°C and, preferably, to between approximately 130 and approximately 220°C until a crystalline compound is obtained.

20 After having been used as catalytic bases in the process in accordance with the present invention, the raw synthetic mordenites have to be subjected to a certain number of modifications that, in particular, are intended:

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Table I

2 theta (°)	d <sub>hkl</sub> (Å)	I/I <sub>0</sub>
6.38	13.84	mF
8.50	10.39	mf
9.60	9.21	F
13.38	6.61	mF
13.70	6.46	m
14.35	6.17	ff
15.10	5.86	f
19.48	4.55	mF
20.72	4.28	ff
22.15	4.01	F
23.00	3.86	ff
23.50	3.78	f
24.30	3.66	ff
25.55	3.48	FF
26.20	3.398	F
27.65	3.223	mF
30.75	2.905	m
32.60	2.744	ff
33.08	2.706	ff
34.93	2.566	ff
35.55	2.523	f
40.39	2.231	ff
44.3	2.088	f

- to eliminate any organic compounds that are possibly present in the solid after synthesis;
- to eliminate the major part of the sodium cations and to replace them by protons;
- to optimize the overall Si/Al atomic ratios and the structural skeleton [of the mordenite material].

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In order to attain these objectives, use can be made, as follows, of any technique that is known to the technical expert.

- 10      \*      In order to eliminate the organic compounds that are possibly present in the mordenite after its synthesis in a fluoride medium, calcination can be carried out at a temperature of at least 350°C and, preferably, at least 450°C and, for example, between 500 and 600°C, for a period of at least 10 minutes and, preferably, for between 30 and 180 minutes in the presence of e.g. at least 1% and, preferably, at least 5% of oxygen.
- 15      \*      In order to eliminate the major part of the sodium cations, one or more series of exchanges can be carried out, for example, in solutions of an ammonium salt (the chloride, nitrate, sulfate, etc.) at an ammonium [ion] concentration of, generally, between 0.01 and 15 N (or in various solutions of acids (HCl, H<sub>2</sub>SO<sub>4</sub>, HNO<sub>3</sub>) of slightly elevated normality) at a temperature between 10 and 180°C (with exchange optionally under
- 20      autogenic pressure) over a period of more than approximately 10 minutes.
- 25      \*      In order to obtain the overall Si/Al atomic ratios and the structural skeleton [of the mordenite material] that are desired, recourse may be had to techniques for the removal of aluminum that are known to the technical expert such as, for example, direct acid attack on the NaM form, which has been exchanged partially or not at all using H<sup>+</sup> or NH<sub>4</sub><sup>+</sup>, and calcination of the NH<sub>4</sub>M or HM form, optionally in the presence of steam, whereby this is preferably followed by a chemical treatment of the type involving attack by an acid (M = mordenite). The acid attack comprises at least one treatment in solutions of an acid of various types (HCl, HNO<sub>3</sub>, H<sub>2</sub>SO<sub>4</sub>, HF, etc.) at temperatures that are between 10 and
- 30      150°C (with the attack optionally under autogenic pressure). The concentrations with respect to acid are between 0.1 and 15 N and, preferably, between 5 and 12 N. The ratios

by volume of the solution to the weight of the dry solid are between 3 and 20 cm<sup>3</sup>/g and, advantageously, between 3 and 7 cm<sup>3</sup>/g. The duration of the treatment is at least 10 minutes. In order to attain the desired specifications, recourse can be had to a limited number of attacks by acids, which are carried out under severe conditions, or to a larger number of attacks that are carried out under moderated conditions. The direct acid processing of the mordenite that had been synthesized in a fluoride medium can also permit the elimination of the major part of the sodium cations and thus avoid the prior step of cation exchange. Thermal processing in the presence of steam usually comprises calcination that is carried out at a temperature that is greater than 350°C and, preferably, greater than 500°C, over a period of at least 10 minutes under an atmosphere that contains at least 1% of steam and, preferably, at least 10% of steam. The acid attack, which optionally follows calcination, is carried out under the same conditions as the acid attack that was described in the preceding sections.

The process for the production of a mixture of 2-phenylalkanes and 3 phenylalkanes in accordance with the invention comprises the reaction of benzene, in a reaction zone, with a charge, which contains at least one linear olefin that comprises 9 to 16 and, preferably, 10 to 14 atoms of carbon in its molecule and that is in contact with at least one catalyst that is based on a mordenite that is prepared from the raw synthetic mordenite that was synthesized in a fluoride medium and that was described previously, whereby the said mordenite (that forms the basis of the said catalyst) has the following physicochemical properties:

- an overall atomic ratio of Si/Al of between 6 and 100 and, preferably, between 15 and 60 and, still more preferably, between 20 and 50;
- a concentration by weight with respect to sodium that is less than 1,000 ppm and, preferably, less than 500 ppm;
- a unit cell volume that is less than 2.781 nm<sup>3</sup> (1 nm = 10<sup>-9</sup> m) and, preferably, less than 2.748 nm<sup>3</sup>;
- an asymmetrical vibration frequency of the TO<sub>4</sub> tetrahedra (T = Al or Si) that is greater than 1,076 cm<sup>-1</sup> and, preferably, greater than 1,080 cm<sup>-1</sup> in the infrared spectrum;
- a micro-porous volume that is greater than 0.160 cm<sup>3</sup> (liquid)/g or, preferably, greater

than  $0.180 \text{ cm}^3$  (liquid)/g, whereby this volume is measured via the adsorption of nitrogen at 77 K under a partial pressure of nitrogen of 0.19 [undefined units].

Without binding ourselves to a particular theory, it is probable that the superior levels of performance of the mordenites that are used in the invention result, at least in part, from the distribution of the aluminum of the structural skeleton at the location of the 4 non-equivalent crystallographic sites that comprise this structural skeleton. In fact, the catalytic properties of the zeolites are mainly linked to their acidic properties. These are determined by the exact localization of the aluminum of the structural skeleton as well as by the Si/Al atomic ratios of the structural skeleton and overall. In a classical mordenite (synthesis in an  $\text{OH}^-$  medium), it is known that the aluminum [atoms] of the structural skeleton are mainly located in rings of 4 tetrahedra with a structure in the form of Al-O-Si-Al pairs (V. GRAMLICH, PhD Dissertation, ETH No. 4633, Zurich, 1971; G. DEBRAS, J.B. NAGY, Z. GABELICA, P. BODART, P.A. JACOBS, Chem. Lett. 1983, p. 199). This configuration is additionally favored thermodynamically (E.G. DEROUANE, J.G. FRIPIAT, Proc. 6th. Int. Zeolite Conf., Reno, USA, 1984, p. 717). The presence of these aluminum pairs is favorable to bi-site reactions, such as dismutation and transalkylation reactions as well as coking reactions. This type of reaction is undesirable in the case of the alkylation of benzene via linear olefins. In fact, limitation of coking is sought so as to ensure a maximum cycle time for the catalyst; the dismutation and transalkylation reactions are also to be limited as much as possible in order to maximize the production of 2-phenylalkanes and 3-phenylalkanes per pass. The distribution of the aluminum [atoms] of the structural skeleton is different in the mordenites that are used in the invention: these aluminum pairs are definitely absent or, at the very least, they are present in very limited quantities and this induces acidic properties and thus different catalytic properties.

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In the present invention, the mordenite that was defined in the preceding sections can be used on its own or in the form of a mixture with a binder or a matrix that is generally selected from the group that comprises the clays, [the various types of] alumina, silica, magnesia, zirconia, titanium oxide, boron oxide and any combination of at least two of the said compounds, such as silica/alumina, silica/magnesia, etc. All the methods that are known for agglomeration and molding are applicable, such as e.g. extrusion, pastille formation, coagulation in the form of

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drops, drying by atomization, etc.

Thus in the process in accordance with the invention, use is made of at least one catalyst, which is based on a mordenite that has the characteristics that were defined in the preceding sections (and, in particular, that it is prepared from a mordenite that had been synthesized in a fluoride medium), whereby the catalyst generally contains 1 to 100% and, preferably, 20 to 98% and, for example, 40 to 98% by weight of the said mordenite, and 0 to 99% and, preferably, 2 to 80% and, for example, 2 to 60% by weight of a matrix.

In accordance with a preferred variant of the process in accordance with the invention, benzene is made to react, in a reaction zone, with a charge that contains at least one linear olefin that comprises 9 to 16 atoms of carbon and, preferably, 10 to 14 atoms of carbon in its molecule and that is in contact with at least one catalyst that is based on a mordenite that has the characteristics that were defined in the preceding sections (alkylation reaction); the product that is obtained is then fractionated in such a manner as to recover separately a first fraction, which contains the non-converted benzene, a second fraction, which contains at least one non-converted C<sub>9</sub>-C<sub>16</sub> (and preferably C<sub>10</sub>-C<sub>14</sub>) linear olefin, a third fraction, which contains the 2-phenylalkanes and 3-phenylalkanes, and a fourth fraction that contains at least one polyalkylbenzene (or polyalkylbenzene fraction), whereby this is then recycled, at least in part, back into the said reaction zone where it then reacts with benzene in contact with the said catalyst, i.e. the catalyst that was mentioned above and that is based on the mordenite that was defined in the preceding sections, in order to be transalkylated (transalkylation reaction) at least in part, and a mixture of 2-phenylalkanes and 3-phenylalkanes is recovered.

This variant of the invention is thus characterized, in particular, by the fact that the alkylation and transalkylation reactions take place conjointly in the same reaction zone (i.e. in the same reactor) in the presence of the same catalyst.

The first fraction, which contains non-converted benzene that arises from the alkylation reaction, is preferably recycled, at least in part, back into the said reaction zone: thus at least part of the benzene, which reacts with at least part of the fourth recycled fraction (or

polyalkylbenzene fraction), comprises benzene that has not been converted during the alkylation reaction, i.e. non-converted benzene that arises from the said first fraction.

5 In addition, the second fraction which contains at least one non-converted C<sub>9</sub>-C<sub>16</sub> (and usually C<sub>10</sub>-C<sub>14</sub>) linear olefin that arises from the alkylation reaction is preferably recycled, at least in part, back into the said reaction zone.

10 The recycled part of the fourth fraction preferably contains, in essence, at least one dialkylbenzene and it is preferably essentially free from heavy alkylaromatic compounds that can be eliminated by fractionation if required.

The mixture of 2-phenylalkanes and 3-phenylalkanes that is obtained in accordance with the invention is advantageously nearly free, or essentially free, from n-phenylalkanes, whereby n is a whole number that is greater than or equal to 4.

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The sole diagram illustrates one particular form of embodiment of the invention.

Fresh benzene (pipe 1) is mixed, on the one hand, with a mixture (pipe 2) of benzene and C<sub>10</sub>-C<sub>14</sub> linear olefins (a fraction whose distillation range is between 165 and 240°C), whereby  
20 the benzene proceeds, via the pipe 15, from the head of the first fractionating column 14 and the said C<sub>10</sub>-C<sub>14</sub> olefins proceed, via the pipe 18, from the head of the second fractionating column 17 and, on the other hand, [this fresh benzene is mixed] with a mixture (pipe 3) of "fresh" C<sub>10</sub>-C<sub>14</sub> linear olefins, which arrive via the pipe 4, and dialkylbenzenes which proceed, via the pipe 24, from the base (pipe 22) of the third fractionating column 20 after optional purging (pipe 23).  
25 The entire mixture (or charge) that is obtained is then sent, via pipe 5, into the heat exchanger 6 where it is preheated via heat exchange with the effluent that is being discharged from the alkylation reactor 11 via the pipe 12. After its period of residence in the heat exchanger 6, the mixture is then sent into the alkylation reactor 11 via the pipe 7. If the preheating in the heat exchanger 6 is insufficient, then the mixture that leaves this exchanger 6 is optionally sent, in  
30 advance via pipe 8, into the heating unit 9 from where it leaves again via the pipe 10 and is directed toward the alkylation reactor 11. At the outlet of the reactor 11, the effluent is sent, via

the pipe 12, to the heat exchanger 6 and then it is sent, via the pipe 13, to the first fractionating column 14. The excess benzene, which has not reacted, is drawn off, via the pipe 15, at the head of this first fractionating column 14, whereby this benzene is then recycled - after mixing with the non-transformed  $C_{10}$ - $C_{14}$  linear olefins that proceed, via the pipe 18, from the head of the second fractionating column 17 - back to the inlet of the reactor 11 via the pipe 2. A mixture is recovered at the base of this first fractionating column 14 and this mixture is sent, via the pipe 16, to the second fractionating column 17. The non-transformed  $C_{10}$ - $C_{14}$  linear olefins are recovered, via the pipe 18, at the head of this second fractionating column 17 and these linear olefins are then recycled - after mixing with benzene that proceeds, via the pipe 15, from the head of the first fractionating column 14 - back into the inlet of the reactor 11 via the pipe 2. A mixture is drawn off at the base of this second fractionating column 17 and this mixture is sent, via the pipe 19, to a third fractionating column 20. A mixture of 2-phenylalkanes and 3-phenylalkanes (a fraction whose distillation range is between 290 and 370°C) is recovered, via the pipe 21, at the head of this third fractionating column 20 and this mixture is sent to the storage system. Dialkylbenzenes are drawn off, via the pipe 22, at the base of this third fractionating column 20, whereby at least a large major part of these dialkylbenzenes is recycled, via the pipe 24, back into the reactor 11 and a small quantity of these dialkylbenzenes is optionally purged from the circuit via the pipe 23.

The process in accordance with the invention can be carried out at a temperature that is less than 400°C and, preferably, less than 60°C at a pressure of 1 to 10 MPa using a flow rate of liquid hydrocarbons (spatial velocity) of approximately 0.5 to 50 volumes per volume of catalyst per hour with a molar ratio of benzene/( $C_9$ - $C_{16}$ ) linear olefin(s) that is between 1 and 20.

The following examples illustrate the invention though without thereby limiting its scope.

#### EXAMPLE 1 Preparation of three catalysts A, B and C

The raw material that is used is a mordenite (free from organic compounds) that had been synthesized in a fluoride medium in accordance with the preparation procedure that is described in French patent application 89/13317.

100 grams of this mordenite in its sodium form are divided into three equal parts  $A_0$ ,  $B_0$  and  $C_0$  that are each subjected to acid attack with the help of aqueous solutions of nitric acid with a normality of 4.5 N, 10 N and 14 N, respectively, over a period of 4 hours for the attack by the 4.5 N acid and over a period of 6 hours for the attack by the 10 N and 14 N acids: in this way, each solid is refluxed in the aqueous solution of nitric acid using a ratio of the aqueous nitric acid, by volume, to the dry mordenite, by weight, (V/W) that amounts to 5.4 and 5 cm<sup>3</sup>/g, respectively, and then it is washed with water.

The characteristics of the mordenites  $A_1$ ,  $B_1$  and  $C_1$ , which are obtained, are presented in Table II.

Table II

	$A_1$	$B_1$	$C_1$
Na (ppm by weight)	200	50	10
Si/Al (overall atomic [ratio])	10	45	98
Unit cell volume (nm <sup>3</sup> )	< 2.733	< 2.733	< 2.733
Infrared TO <sub>4</sub> frequency (cm <sup>-1</sup> )	> 1080	> 1080	> 1080
Micro-porous volume (cm <sup>3</sup> /g) (adsorption of nitrogen)	> 0.160	> 0.160	> 0.160

Each mordenite  $A^1$ ,  $B^1$  and  $C^1$  that was prepared in the preceding sections is then mixed with alumina gel. Each mixture that is obtained is then brought into the form of extruded [filaments] with a diameter that is equal to approximately 1.8 mm by passing it through an orifice in a plate. The extruded [filaments] are then dried in an oven at 120°C for one night and then they are calcined in air at approximately 550°C.

Catalysts A, B and C are thus obtained that are based, respectively, on the mordenites  $A_1$ ,



B<sub>1</sub> and C<sub>1</sub> that contain 80% by weight of mordenite and 20% by weight of alumina.

## EXAMPLE 2

5           The three catalysts A, B and C, which were prepared in Example 1, are each tested in terms of the alkylation of benzene via dodecene-1 for the production of 2-phenyldodecanes and 3-phenyldodecanes under the following operating conditions:

- temperature: 50°C;
- 10    -       pressure: 4 MPa;
- an hourly flow rate of the liquid charge that is equal to 3 times the volume of the catalyst;
- benzene/dodecene-1 molar ratio: 5:5.

The results that are obtained are presented in Table III.

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## EXAMPLE 3 Preparation of the three catalysts D, E and F

The three catalysts D, E and F, which are based on a mordenite that had been synthesized in an OH<sup>-</sup> medium, are prepared here.

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The raw material that is used is a wide-pore mordenite in its sodium form from the Tosoh company, reference TSZ 600 NAA. Its chemical formula in the anhydrous state is Na.Al(SiO<sub>2</sub>)<sub>5.1</sub> and its sodium content is of the order of 5% by weight.

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100 grams of this powder are refluxed for 2 hours at 100°C in a 4 M solution of ammonium nitrate; the volume of the solution of ammonium nitrate that is involved is equal to four times the weight of the dry mordenite ( $V/W = 4 \text{ cm}^3/\text{g}$ ). This cation exchange operation is re-started 3 times. The concentration of sodium by weight in the product that is obtained is approximately 500 ppm.

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This product is then divided into three equal parts D<sub>0</sub>, E<sub>0</sub> and F<sub>0</sub> that are subjected to acid

attack with the help of aqueous solutions of nitric acid of normality 0.9 N, 4.5 N and 8 N, respectively: in this way, each solid is refluxed in the aqueous solution of nitric acid with a V/W ratio that is equal to 4 cm<sup>3</sup>/g and then it is washed with water.

- 5 The characteristics of the mordenites D<sub>1</sub>, E<sub>1</sub> and F<sub>1</sub>, which are obtained, are presented in Table IV.

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Table III

CATALYST	A	B	C
<u>COMPOSITION OF THE CHARGE</u> (% by weight)			
Benzene	71.7	71.7	71.7
Dodecene-1	28.3	28.3	28.3
<u>COMPOSITION OF THE PRODUCT OBTAINED</u> (% by weight)			
Benzene	62.1	59	59.6
Dodecene-1	-	-	0.6
Isomers of dodecene-1	7	-	-
2-phenyldodecane	18.8	34.1	31.6
3-phenyldodecane	7.4	4.4	4
4-phenyldodecane	2.1	0.3	0.3
5-phenyldodecane	0.8	-	-
6-phenyldodecane	0.4	-	-
Didodecylbenzenes	1.3	2	3.5
Heavy residue	0.1	0.2	0.4
<u>LEVELS OF CONVERSION PER PASS</u>			
Benzene	13.4%	17.7%	16.9%
Dodecene-1	100%	100%	97.8%
<u>SELECTIVITIES RELATIVE TO THE DODECENE-1 THAT IS TRANSFORMED</u>			
2-phenyldodecane	45.4%	82.4%	77.9%
3-phenyldodecane	<del>17.9%</del>	<del>10.5%</del>	<del>9.9%</del>
Total	63.3%	92.9%	87.8%

Table IV

	D <sub>I</sub>	E <sub>I</sub>	F <sub>I</sub>
Na (ppm by weight)	185	25	10
Si/Al (overall atomic [ratio])	13	40	90
Unit cell volume (nm <sup>3</sup> )	2.747	2.715	2.690
Infrared TO <sub>4</sub> frequency (cm <sup>-1</sup> )	1080.2	1086.0	1091.7
Micro-porous volume (cm <sup>3</sup> /g) (adsorption of nitrogen)	> 0.160	> 0.160	> 0.160

5 Each mordenite D<sup>I</sup>, E<sup>I</sup> and F<sup>I</sup> that was prepared in the preceding sections is then mixed with alumina gel. Each mixture that is obtained is then brought into the form of extruded [filaments] with a diameter that is equal to approximately 1.8 mm by passing it through an orifice in a plate. The extruded [filaments] are then dried in an oven at 120°C for one night and then calcined in the air at approximately 550°C.

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Catalysts D, E and F are thus obtained that are based, respectively, on the mordenites D<sub>I</sub>, E<sub>I</sub> and F<sub>I</sub> that contain 80% by weight of mordenite and 20% by weight of alumina.

#### EXAMPLE 4

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The three catalysts D, E and F, which were prepared in Example 3, are each tested in terms of the alkylation of benzene via dodecene-1 for the production of 2-phenyldodecanes and 3-phenyldodecanes under operating conditions that are identical to those used in Example 2.

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The results obtained are presented in Table V.

Upon comparing the results that are illustrated in Tables III and V, it can be seen that it is

preferable to work with the catalysts that are recommended by the invention, i.e. that it is necessary to use mordenites that are prepared from mordenites that have been synthesized in a fluoride medium; for the overall Si/Al atomic ratios [in question] (case A and D, B and E, C and F), in fact, the catalysts that are recommended by the invention (A, B and C) provide a  
5 selectivity, in terms of 2-phenyldodecanes and 3-phenyldodecanes, that is much higher (6 to 8 points) than that obtained with the catalysts that are based on mordenite that had been synthesized in an OH<sup>-</sup> medium (D, E and F); moreover, for neighboring overall Si/Al atomic ratios, the activity of the catalysts A, B and C is also found to be better than that of the catalysts D, E and F.

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Finally, reading the results that have been presented in Table III shows that, among the catalysts that are recommended by the invention, it is advantageous to work with a catalyst that is based on a mordenite with an overall Si/Al atomic ratio that is between 15 and 60 (the case with catalyst B) and that exhibits a level of activity and, above all, selectivity that are still better in  
15 terms of 2-phenyldodecanes and 3-phenyldodecanes.

#### EXAMPLE 5

By operating in accordance with the process of the invention in conformity with the sole  
20 diagram, i.e., in particular, by recycling the didodecylbenzenes and the benzene back into the alkylation reactor that contains catalyst B that was prepared in Example 1, a total selectivity of 98.5% is obtained in terms of the 2-phenyldodecanes and 3-phenyldodecanes relative to the transformed dodecene-1. In this way, a mixture of 2-phenyldodecanes and 3-phenyldodecanes is obtained with very high selectivity and this leads to detergents of very high quality that are  
25 perfectly biodegradable.

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Table V

CATALYST	D	E	F
<u>COMPOSITION OF THE CHARGE</u> (% by weight)			
Benzene	71.7	71.7	71.7
Dodecene-1	28.3	28.3	28.3
<u>COMPOSITION OF THE PRODUCT OBTAINED</u> (% by weight)			
Benzene	62.6	59.4	61.3
Dodecene-1	-	-	3.1
Isomers of dodecene-1	7.9	-	-
2-phenyldodecane	14.4	31.4	26.6
3-phenyldodecane	8.6	4.4	3.3
4-phenyldodecane	2.7	0.4	0.4
5-phenyldodecane	1.3	-	-
6-phenyldodecane	0.5	-	-
Didodecylbenzenes	1.8	4.1	4.4
Heavy residue	0.2	0.3	0.9
<u>LEVELS OF CONVERSION PER PASS</u>			
Benzene	12.7%	17.2%	14.5%
Dodecene-1	100%	100%	89%
<u>SELECTIVITIES RELATIVE TO THE DODECENE-1 THAT IS TRANSFORMED</u>			
2-phenyldodecane	34.7%	75.8%	72.1%
3-phenyldodecane	20.8%	10.6%	8.9%
Total	55.5%	86.4%	81%

## Claims

1 - Process for the production of a mixture of 2-phenylalkanes and 3-phenylalkanes in which benzene is made to react, in a reaction zone, with a charge that contains at least one linear olefin that comprises 9 to 16 atoms of carbon in its molecule and that is in contact with at least one catalyst that is based on a mordenite and that has an overall Si/Al atomic ratio of between 6 and 100 and a concentration by weight with respect to sodium that is less than 1,000 ppm and a unit cell volume that is less than  $2.781 \text{ nm}^3$  and an asymmetrical vibration frequency of the  $\text{TO}_4$  tetrahedra ( $\text{T} = \text{Al}$  or  $\text{Si}$ ) that is greater than  $1,076 \text{ cm}^{-1}$  in the infrared spectrum and a microporous volume that is greater than  $0.160 \text{ cm}^3$  (liquid)/g, whereby this volume is measured via the adsorption of nitrogen at 77 K under a partial pressure of nitrogen of 0.19 [undefined units], whereby the said mordenite has additionally been prepared from a mordenite that had been synthesized in a fluoride medium; process in which the product that is obtained is then fractionated in such a manner as to recover separately a first fraction, which contains the non-converted benzene, and a second fraction, which contains at least one non-converted linear olefin with 9 to 16 atoms of carbon in its molecule, and a third fraction, which contains a mixture of 2-phenylalkanes and 3-phenylalkanes, and a fourth fraction, which contains at least one polyalkylbenzene, whereby this fourth fraction is then recycled, at least in part, back into the said reaction zone where it reacts with benzene in the presence of the said catalyst in order to be transalkylated, at least in part, and a mixture of 2-phenylalkanes and 3-phenylalkanes is recovered.

2 - Process in accordance with Claim 1, in which the said mordenite has an overall Si/Al ratio that is between 15 and 60.

3 - Process in accordance with one of the Claims 1 and 2, in which the said mordenite is such that:

- its overall Si/Al atomic ratio is between 20 and 50;
- its concentration by weight with respect to sodium is less than 500 ppm;
- its unit cell volume is less than  $2.748 \text{ nm}^3$ ;

- the asymmetrical vibration frequency of the  $\text{TO}_4$  tetrahedra ( $\text{T} = \text{Al}$  or  $\text{Si}$ ) is greater than  $1,080 \text{ cm}^{-1}$  in the infrared spectrum;
- its micro-porous volume is greater than  $0.180 \text{ cm}^3$  (liquid)/g, whereby this volume is measured via the adsorption of nitrogen at 77 K under a partial pressure of nitrogen of 0.19 [undefined units].

4 - Process in accordance with one of the Claims 1 to 3, in which the mordenite, which had been synthesized in a fluoride medium, possesses:

- a) the following approximate general formula:  
 $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot x\text{SiO}_2$ :  
 where x is a number between 9 and 30; and
- b) an x-ray diffraction diagram that is illustrated in Table I of the specification.

5 - Process in accordance with one of the Claims 1 to 4, in which the said first fraction is recycled, at least in part, back into the said reaction zone.

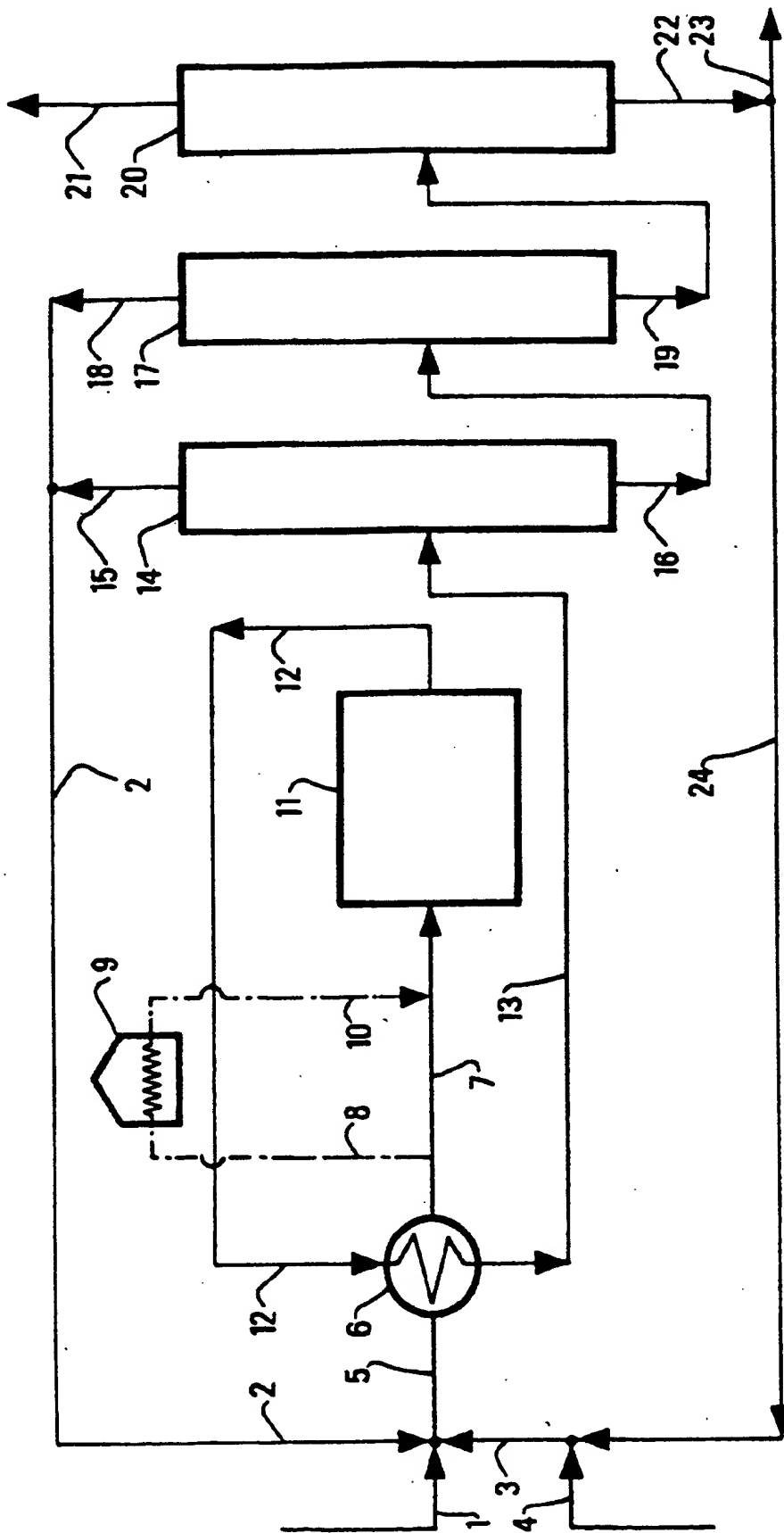
6 - Process in accordance with one of the Claims 1 to 5, in which the said second fraction is recycled, at least in part, back into the said reaction zone.

7 - Process in accordance with one of the Claims 1 to 6, in which the said catalyst additionally contains a matrix that is selected from the group that comprises the clays, [the various types of] alumina, silica, magnesia, zirconia, titanium oxide, boron oxide and any combination of at least two of the said compounds.

8 - Process in accordance with one of the Claims 1 to 7, in which the operating temperature is less than  $60^\circ\text{C}$ .

9 - Use, after sulfonation, of the mixture of 2-phenylalkanes and 3-phenylalkanes, which is obtained by the process in accordance with one of the Claims 1 to 8, as a basis for biodegradable detergents.





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## EUROPEAN RESEARCH REPORT

Application Number  
EP 91 40 1831**DOCUMENTS CONSIDERED TO BE RELEVANT**

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to Claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. <sup>5</sup> )
A	US-A-4 731 497 (GREY)		C07C15/107
A	EP-A-0 366 515 (INSTITUT FRANCAIS DU PETROLE)		C07C2/66
A	FR-A-2 084 704 (UNIVERSAL OIL PRODUCTS)		C11D1/22
			<b>TECHNICAL FIELDS SEARCHED</b> (Int. Cl. <sup>5</sup> )
			C07C
The present search report has been drawn up for all claims.			
<b>Place of search</b>  THE HAGUE		<b>Date research completed</b> OCTOBER 29, 1991	<b>Examiner</b>  J. VAN GEYT
<b>CATEGORY OF CITED DOCUMENTS</b> X: Particularly relevant if taken alone Y: Particularly relevant if combined with another document of the same category A: Technological background O: Non-written disclosure P: Intermediate document		T: Theory or principle underlying the invention E: Earlier patent document but published on, or after, the filing date D: Document cited in the application L: Document cited for other reasons ..... .&: Member of the same patent family, corresponding document	